THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

VOL. 14 FEBRUARY, 1929 No. 2

A COMPARISON OF THE ORE DEPOSITS OF LÅNGBAN, SWEDEN, WITH THOSE OF FRANKLIN, NEW JERSEY.

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Readers of the *American Mineralogist* will recall that quite recently Dr. Flink (1) published in its pages an account of Långban and its minerals. He gives a description of the geology and ore minerals and a list of the very large number of species found there. However, he makes no attempt to describe the genesis of the ores nor does he segregate the numerous and peculiar minerals into paragenetic groups.

The genetic history of these deposits is the principal theme of a paper by Dr. Magnusson (2) which was made available to American readers in a review by Dr. Geijer (2a) in *Economic Geology*. This review does not, however, reproduce the paragenetic table which is of peculiar interest.

The author had the good fortune to spend two days at Långban a few years since under the guidance of Dr. Magnusson. He desires to briefly summarize the facts concerning the Långban mines in order to bring out their similarities to, and differences from those of Franklin. Geijer's review is so concise and clear that it will be quoted in large part; and by reproducing Magnusson's genetic table the details of the mineralogy will be clearly evident.

"The Långban deposit contains iron ores and manganese ores. Although closely associated they are well separated from each other, there being rarely more than two per cent manganese in the iron ores and the same amount of iron in the manganese ore. The country rock is dolomite. Both kinds of ore are clearly replacement deposits. The iron occurs as specular hematite and magnetite. Brick red jasperoid is associated with the hematite, while the magnetite is accompanied by skarn silicates, as diopside, amphibole, and garnet. The magnetite ore and skarn surround the bodies of hematite and jasperoid. The relations clearly indicate that the former association is developed by a recrystallization and alteration of the hematite-jasperoid combination. An early stage in this is marked by the appearance of porphyroblasts of magnetite in the hematite.

"The manganese ore is braunite and hausmannite. The latter is accompanied by a skarn of manganese silicates, pyroxene, amphibole, garnet, and olivine. The relations between braunite and hausmannite (with skarn) form an exact counterpart to those of hematite and magnetite. The development of hausmannite porphyroblasts is well illustrated.

"The parageneses now shown to belong to two distinct periods are explained as follows. At first iron was deposited as oxide, manganese as oxide and partly carbonate, some of which is also still left. With the iron came the silica of the jasperoid. The geological facts admit of no other explanation than that the iron and manganese ores belong to the same period of mineralization. The salient problem, then, is the explanation of their deposition as separate ore bodies. . . . The presence of abundant oxygen appears to account for the separate deposition of iron and manganese, the occurrence of manganese oxide and carbonate but no ferrous carbonate, the presence of lead as silicates instead of sulphide, and of arsenic as acid radicals, etc. Later, a rise of temperature has caused the change of hematite to magnetite, of braunite to hausmannite, and the accompanying skarns.

"Lead, arsenic and antimony occur constantly in all the ores of Långban. Of the lead silicates, kentrolite and melanotekite occur with the primary ores, ganomalite and hyalotekite with the skarn ores. Similarly, the primary arsenate, karyinite is replaced by berzeliite. Therefore, also the lead and arsenic minerals can be divided into those of primary deposition and those of the second or skarn period. The same holds true of the antimony.

"Later than the skarn minerals are the 'fissureminerals' representing a third period . . . . regarded as an end phase of the skarn period. In this group is found a great part of the famous Långban minerals, as arsenites, native lead, pyrochroite, thaumasite, tilasite, margarosanite."

With this very clear picture of the general nature of the Långban deposit before us and with Magnusson's detailed paragenetic table it is possible to get some insight into the development of the remarkable complex of minerals found at Långban. The primary

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replacements were composed of few minerals, the chief ones of very simple composition. The rise of temperature which followed their deposition caused widespread chemical interactions of the original minerals with a great increase in the mineral complexity of the resulting aggregate. Magnusson believes that nothing of importance was added to the deposit after the primary mineralization. Nevertheless several elements appear in the skarn period which were not found in the earlier minerals. Boron in hyalotekite and pinakiolite; beryllium in trimerite and bromellite; chlorine in hedyphane; are suggestive of magmatic additions. The sulphides, too, found in nests in skarn and magnetite appear to be additions. Manganosite and periclase are interpreted as resulting from the breakdown of rhodochrosite and dolomite, respectively.

The third period, that of vein formation, is marked by still greater mineral diversity. The veins are for the most part small gash veins, often with open vugs and generally containing abundant calcite. They are found in skarn, in both types of ore, and especially in the narrow spaces separating iron and manganese ore bodies, so they contain materials drawn from both sources. The author's impression gained during his brief visit to the mine and from the study of many specimens was that the vein material had not travelled far. Many of the minerals have been found in but a single vein or small group of them and Flink's description of the hundreds of specimens which have been preserved for study, in each of which occurs a single mineral or even a single crystal, indicates very local chemical reactions.

There is a noteworthy development of hydrous minerals which is in agreement with the lower temperature assumed by Magnusson to have prevailed during their formation. Barite is abundant and fluorine appears in fluorite and tilasite. Reducing conditions are indicated by the occurrence of native metals, lead especially being found in masses as great as fifty pounds in weight; and by the presence of arsenites like armangite and manganites like quenselite. The multiplicity of lead compounds and of arsenates and silico-arsenates of manganese is the chief feature of the mineralogy of the veins.

The idea has frequently found expression that the Långban deposits have much in common with those of Franklin. It is based on the fact that not only do both deposits consist largely of iron and manganese ores but that a number of rather complex minerals are common to both and are practically unknown elsewhere. Such minerals are shown in the list that follows.

Schefferite = Mn-pyroxene
Manganophyllite = Mn-biotite
Tephroite = Mn-olivine
Manganosite
Pyrochroite
Hedyphane
Barysilite
Margarosanite
Nasonite
Allactite
Dixenite, Långban, close to Mcgovernite, Sterling Hill

If we include with Långban in this comparison the closely similar deposits of manganese ore at Harstigen, Pajsberg and Jacobsberg we may add to this list:

Hyalophane
Caryopilite = bementite of Franklin
Ectropite = bementite of Franklin, probably
Friedelite
Ganophyllite

Those minerals then, common to both deposits, include manganese silicates, oxides, and arsenates; and lead silicates. The list is not impressive. The principal ore minerals of the two localities are different. And there is the important difference that zinc is wholly absent from the Långban ores.

The geological history of the Franklin deposits is more diversified. There is, however, the striking analogy between the two that manganese-rich skarn has formed in great quantity at both, due to an increase in temperature after the primary minerals were implaced; at Långban this rise was apparently regional while at Franklin it was due to contact metamorphism of a local sort. At Långban the rarer elements whose presence led to the formation of a host of minerals, lead, arsenic and antimony, seem to have been introduced with the ore; at Franklin on the other hand the comparable elements, lead, arsenic, chlorine and sulphur, came in with the later pegmatite. If the mineralogical complexity of the two ore deposits is based on the length of the respective mineral lists, there is no great difference between them unless we include the as yet undescribed minerals from Långban in which case the balance lies heavily in favor of the latter. It is of course to be remembered that the deposits in New Jersey are vastly more extensive than those of Sweden so that the mineral richness of Långban is proportionately much more remarkable.

REFERENCES

(1). Långban and its Minerals. Gustav Flink. *Am. Mineral.*, **11,** 195 (1926).

(2). Långbansmineralen fran geologisk synpunkt. N. H. Magnusson. *Geol. Fören. i. Stockholm Forhandl.*, **46,** 284 (1924).

(2a). Review of the same paper. The Långban minerals from a geological point of view. Per Geijer. *Econ. Geol.*, Vol. **19,** 687 (1924).

(3). The Långban Mines. Hj. Sjogren. *Geol. Fören. i. Stockholm Forhandl.*, **32,** 1295 (1910).

This paper which is in English gives much additional material on the geology of the mines, with a map.

Discussion of the foregoing paper would be welcomed by the author and editor and any comments or criticisms received will be printed in a future number of the Journal. The Editor.

CAMSELLITE AND SZAIBELYITE

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Schaller[1] has recently concluded that camsellite and szaibelyite are probably identical, since they seem to be very similar both chemically and optically, so far as can be inferred from published descriptions. His summary of the chemical analyses serves to show that the two minerals are at least similar in chemical composition. His summary of the optic properties leads to an analogous conclusion, but unfortunately it is incomplete in regard to the available optic data for camsellite.[2] In a description of szaibelyite published recently[2] the writer made no attempt to select the correct optic data but stated that published data are very inconsistent; Schaller's corrected data[3] make it very probable that szaibelyite is uniaxial and negative with $N_o = 1.65\pm$ and $N_e = 1.58\pm$, as reported recently by Gillson and Shannon.[4] Therefore it is important to describe in some detail the evidence for the statement[2] that the optic angle of camsellite is large.

On account of the fact that the original description[5] of camsellite did not include any measure of N_m nor of the optic angle, the writer obtained a small fragment of the type material through the courtesy of Dr. Ellsworth. A study of this material was undertaken by R. H. B. Jones and C. H. Stockwell. It was found to be in the form of microscopic lath-shaped crystals with X parallel with the elongation and Y normal to the laths. In order to measure N_m by the immersion method it was necessary to turn one of these laths on edge. To accomplish this Mr. Jones used an ingenious device. One of the laths was inserted in a capillary glass tube of the proper size and this tube was placed lengthwise on an object glass previously prepared for it by cementing on its upper surface two rectangular strips of cover glass large enough to cover the object glass, except for a narrow space between the strips, as shown in Fig. 1. A suitable immersion liquid was allowed to fill the capillary tube, and the same liquid was used to fill the space between the tube and the surrounding glass plates (including a cover glass placed over the tube). A magnified section through the apparatus is shown in Fig. 2. Then, since the tube was somewhat longer than the cover glass, it was easy to turn the tube, and thus turn the lath-shaped crystal, so as to set it on edge with respect to the microscope. In this way it was found that the index of the crystal, for light vibrating normal to the elongation varied decidedly during rotation of the crystal about its long axis. In fact, the index was 1.649 when the lath was lying flat with respect to the object glass and 1.620 ± 0.005 when the lath was set on edge. Assuming no error in this determination of N_m, the optic angle (2V) must be nearly 80°, since $N_p = 1.575$. Therefore camsellite is biaxial (and negative) with a large optical angle. According to the best data now available, szaibelyite is uniaxial. Therefore the two minerals cannot be the same even if there is no chemical difference between them, a condition which is not yet fully proved.

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[1] W. T. Schaller, *Amer. Mineral.*, **XIII**, 1928, p. 230.

[2] See A. N. Winchell, *Optical Mineralogy*, Part 2, **1927**, p. 93.

[3] The incorrect data for N_o and N_e of szaibelyite were unfortunately repeated from *Zeit. Krist.*, **LX**, 1924, pp. 162, 163, 170 in the writer's *Optical Mineralogy*, part 2, **1927**, p. 93.

[4] *Amer. Mineral.*, **X**, 1925, p. 137.

[5] H. V. Ellsworth and E. Poitivin, *Trans. Roy. Soc. Canada*, **XV**, 1921, p. 145.

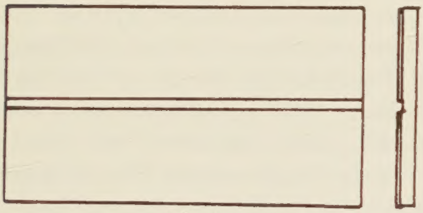

Fig. 1

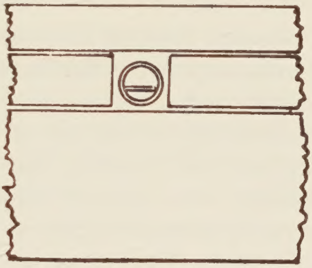

Fig. 2

FIG. 1.

Object glass with two strips of cover glass cemented to surface. True size.

FIG. 2.

Magnified vertical section through a capillary tube between two pieces of cover glass. The tube rests on an object glass and has a cover glass over it; it contains a lath-shaped crystal.

Through the courtesy of Dr. Ellsworth in supplying type material Messrs. Jones and Stockwell were able to measure the indices of sussexite by the same method and thus determine that it is biaxial and negative with a small optic angle. Their results on sussexite were as follows: $N_g = 1.712 \pm 0.003$, N_m slightly higher than 1.70, $N_p = 1.6388$, $N_g - N_p = 0.073$.

PSEUDO-CUBIC QUARTZ CRYSTALS FROM ARTESIA, NEW MEXICO

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Quartz crystals are among the most wide-spread of crystal forms, especially the hexagonal prism terminated by the two rhombohedral forms *r* and *z*. However, quartz crystals consisting dominantly of but one of the rhombohedral forms are rare and known from relatively few localities. This paper describes a new locality, near Artesia, New Mexico, where rhombohedral quartz crystals of large size are to be found. These crystals closely simulate cubes. They occur with other crystals of more common habit, and here, and in numerous other localities in southeastern New Mexico, where the common quartz crystals occur, they are known as "Pecos diamonds."

The senior author has observed that the initial form of some doubly terminated quartz crystals[1] occurring in gypsum near Acme, New Mexico (some 65 miles north of Artesia) was the plus rhombohedron. None of these crystals attained a size greater than 0.15 millimeter. From one of his associates, Mr. E. M. Hawtof of the Texas Bureau of Economic Geology, the junior author learned of the occurrence of great numbers of quartz crystals in gypsum near Artesia. He visited the area in March, 1928, the locality being along the last bluff on the Pecos river, five miles east of Artesia, New Mexico. The quartz crystals are most abundant along the bluff from the bridge over the Pecos river to a point some three miles south.

The gypsum beds in which they occur belong in the red beds of that region. They lie above the San Andreas formation and probably belong in the Chupadera group. The series consists of alternating beds of massive white gypsum and red sandy shale.

The crystals have weathered out of the gypsum, and, in some places, occur by the million; in others, are much less abundant. The crystals can be seen in place in numerous exposures along the bluff. They are in greatest abundance in a zone at the top of a gypsum bed and just below the red sandy shale. At one locality, some three miles below the bridge, the upper four inches of the gypsum bed is literally a mass of quartz crystals. They occur below this zone but are less abundant there.

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[1] Tarr, W. A. Doubly Terminated Quartz Crystals in Gypsum from Acme, New Mex. *Am. Mineral.*, **14**, 19–25, 1929.

The majority of the crystals are pink, red, or dark red, and the remainder (not to exceed 10 per cent) are white or colorless. The color of the crystals is, in large part at least, dependent upon the color of the gypsum. Those crystals occurring near the contact of the gypsum with the red shale are decidedly darker colored than those below. In one specimen of gypsum, a pink band extended across the specimen, evidently following a joint. Two quartz crystals had developed along this band; one, wholly within it, was pink; the other, only partly within it, was pink where it was in the colored band, and colorless where it lay outside it. Crystals in the white gypsum were not colored. In this case, the coloring material, hematite, had been introduced into the gypsum first and then the quartz was deposited. The irregular distribution of the color in the quartz is in keeping with its irregular distribution in the gypsum. In the occurrence near Acme, described by the senior author, the source of the hematite in the quartz crystals was the gypsum, into which it has been introduced from the overlying red members of the series.

The quartz crystals, as found on the surface and in place, are dominantly quartzoids or doubly terminated prisms, but among these there are a considerable number (possibly two per cent) of pseudo-cubic or rhombohedral forms (Figure 1). In a selected collection of crystals, the pseudo-cubic forms constitute nearly 20 per cent of the total collection. Radiating aggregates occur, but are not common. Quartzoids are especially common, and occur in all sizes up to four cm. in length, the average being about two cm. Some are perfect and others show a narrow zone of prismatic faces. The pseudo-cubic crystals are equidimensional, the largest being about one cm. across. The prismatic forms rarely exceed two cm. in length and are from six to eight mm. in thickness.

The rhombic or pseudo-cubic forms are of especial interest. The development of the plus rhombohedron *r* on crystals of one cm. in size, with the almost complete absence of the minus rhombohedron *z*, or at best with it only moderately developed, is rare. Crystals with the form *r* much larger than *z*, but singly terminated, are found, but they do not have the pseudo-cubic habit. This habit results from the fact that the angle between the faces of the rhombohedron r is 85° 46′, thus closely approaching a cubic form.

When the minus rhombohedron z is present, it modifies the corners of the plus form. The two faces differ in luster, the plus form being the most brilliant. Etching of the crystals revealed the fact that the distribution of the etch pits was not in strict conformity with the position usually obtained by etching, but instead, the pits were in bands that covered the surface irregularly. Definitely orientated etch pits, such as those secured on vein quartz, were not produced on these crystals.

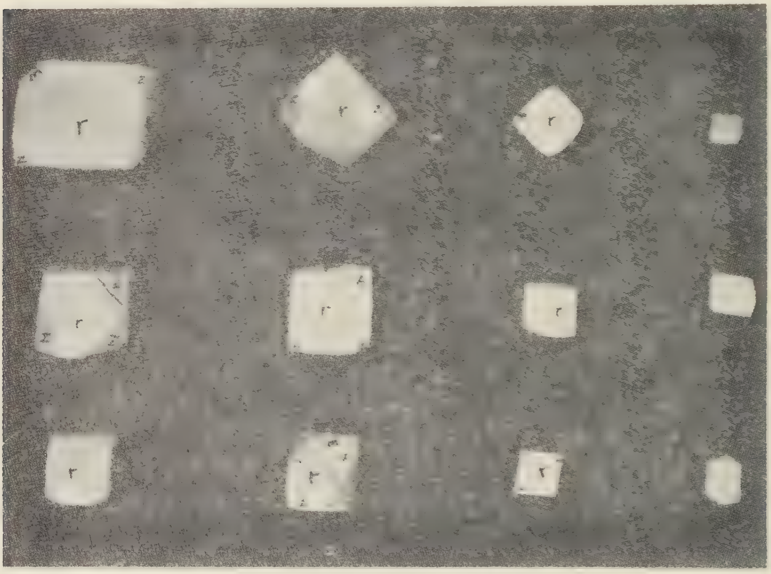

Fig. 1.

Pseudo-cubic Quartz Crystals. Natural size. Counting from the left, number 3 in the top row, numbers 2 and 4 in the second row, and 2 and 3 in the third row have been etched with hydrofluoric acid. r = plus rhombohedron, z = minus rhombohedron, m = prism.

In the senior author's paper on the quartz crystals found near Acme, the initial form was the plus rhombohedron r. When they attained a size of 0.15 mm. they began to develop the minus form z and soon become quartzoids. These large rhombohedral forms from Artesia indicate the presence of an inhibiting factor that prevented the development of the minus form. This factor was evidently of local distribution for the rhombohedral forms occur along with the other forms but in minor numbers.

What, then, could this inhibiting factor have been? The gypsum probably had no effect. Since the rhombohedral forms were colored by iron oxides just as the other forms were, the presence of the coloring matter was evidently not a factor. The concentration of the solution introducing the silica may have been a factor as well as its composition. An excess of one alkali over the other, or the presence of Mg ions (Mg ions are excellent coagulating agents for silica) might have influenced the development of the plus form or have inhibited the development of the minus form. It is also possible that the form assumed may be due to the character of the electrolyte, a strong positive electrolyte producing one form, and a weak positive electrolyte the other. The determination of the factors controlling the development of the two rhombohedrons offers an interesting field of investigation, but one beset with considerable difficulty for quartz is not readily precipitated as such, but rather as a gel.

NEW DATA ON ATOMIC DIMENSIONS

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In a review of a paper by V. M. Goldschmidt[1] attention was called to the fact that new values for atomic dimensions are coming to be accepted, and a summary of some recent work along this line may be worth publishing here. By means of X-rays it is possible to measure with a high degree of accuracy the distances between the centers of layers of atoms in crystals, and, whenever the arrangements of atoms in these layers can be worked out, the distances between the centers of adjacent atoms can be calculated. Until recently, however, there has been a considerable difference of opinion as to what fraction of the distance is assignable to each member of the pair of atoms. In halite, for example, the distance between Na and Cl centers is known with precision to be 2.814 am. units,[2] but what proportion of this length may be regarded as representing the radius of the sodium, and what the chlorine, remains to be determined.

On the basis of some reasonable though admittedly empirical assumptions as to the refractive powers of atoms, Goldschmidt[3] has calculated effective radii of a large number of atoms in variously charged conditions, and Pauling,[4] on the basis of modern wave-mechanics theories of electron arrangement, has presented theoretical values for most of the same elements, the two series of data agreeing well in many cases. The radius values deduced in these studies, with a few from other sources, are listed in table 1. The elements are arranged in the order of their atomic numbers and data are given for three different conditions, namely positively charged, neutral, and negatively charged (the first and last being termed ions). In many instances the radii for each condition given by different methods of calculation or by measurements on different classes of compounds show some divergence, so instead of a single value a range is stated. The theoretical wave-mechanics values are placed in bold-face type, and the values considered non-typical are surrounded by parentheses. For example, the 14th line in the table reads: 14 Si^{+4} (0.22–) 0.39–**0.41.** Si° (1.12–) 1.18. Si^{-4} (1.98); **2.71.** This signifies first, that the element with atomic number 14, silicon, when carrying 4 positive charges, has an apparent radius of between 0.22 and 0.41, but that the lower values are obtained from compounds in which the atoms appear to be deformed or otherwise abnormal, so Goldschmidt gives 0.39 as most significant, while wave-mechanics theory yields 0.41. Second, when neutral this atom's radius ranges from 1.12, in abnormal compounds, to 1.18 in those regarded as typical. And third, when carrying 4 negative charges, the value is 1.98, according to calculations deemed faulty, but 2.71 according to the theory.

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[1] *Am. Mineral.*, 12, 28–31 (1927).

[2] Atomic dimensions are commonly stated in units of 10^{-8} cm., often called ångström units; as, however, the initial character in this word is difficult to get set in type and to pronounce, in this country, I prefer to substitute the symbol *am.*, which may be regarded as an abbreviation of "atom-meter."

[3] Geochemische Verteilungsgesetze der Elemente. VII. Die Gesetze der Krystallochemie. *Skr. Norske Vidensk. Akad. Oslo I. Mat.-Nat. Kl.* No. 2, 117 pages, 1926. This paper, together with the other members of the series, I to VIII, represents the most important contribution to chemical crystallography and geochemistry of recent years.

[4] *J. Am. Chem. Soc.*, 49, 765–790 (1927).

In applying the data of table 1 to the study of replacements in minerals and of similar problems, it should be borne in mind that in halides and oxides the atoms are usually ionized, so that the values in the outer columns apply. Thus in fluorite the value for Ca^{+2} should be added to that for F^{-1}, giving between 2.32 and 2.42, depending on which ends of the range are used, or 2.37 as a mean; and the observed Ca – F distance in the crystal is 2.36 am. Again, in rutile, Ti^{+4} added to O^{-2} gives 1.96–2.08, mean 2.02, and the observed Ti – O distance is 1.98 am. In the remaining types of compounds, on the other hand, the atoms appear to be largely neutral, so the values in the central column are to be used. In sphalerite, for example, the mean of the sum of the radii of Zn° and S° is 2.36, and the observed Zn – S distance 2.35. The relations in the silicates remain to be worked out—it being possible that in them some atoms are ionized and others not—but it may be noted in passing that in this set of radius values, sodium and calcium lie very close together, and barium and potassium even closer, in both positive ion and neutral columns, lending support to the view that atomic size has something to do with the replaceability observed in these element-pairs.

TABLE I. EFFECTIVE RADII OF ATOMS, IN AM. UNITS.

1					H^{-1}	(1.27); **2.08.**
2			He°	(0.93).		
3	Li^{+1}	**0.60**–0.78(–0.82).	Li°	(1.50–)1.56.		
4	Be^{+2}	**0.31**–0.34.	Be°	1.05(–1.15).		
5	B^{+3}	**0.20.**				
6	C^{+4}	**0.15.**	C°	(0.45–)0.77.	C^{-4}	**2.60.**
7	N^{+5}	**0.11.**	N°	(0.65–)0.71.	N^{-3}	**1.71.**
8	O^{+6}	**0.09.**	O°	0.60(–0.65).	O^{-2}	1.32–**1.40.**
9	F^{+7}	**0.07.**	F°	0.67.	F^{-1}	1.33–**1.36.**
10			Ne°	(1.12).		
11	Na^{+1}	**0.95**–0.98(–1.09).	Na°	(1.77–)1.86.		
12	Mg^{+2}	**0.65**–0.78(–0.85).	Mg°	(1.42–)1.62.		
13	Al^{+3}	**0.50**–0.57(–0.66).	Al°	(1.16–)1.43.		
14	Si^{+4}	(0.22–)0.39–**0.41.**	Si°	(1.12–)1.18.	Si^{-4}	(1.98); **2.71.**
15	P^{+5}	**0.34.**	P°	0.93	P^{-3}	**2.12.**
16	S^{+6}	**0.29**–0.34.	S°	1.02–1.04.	S^{-2}	1.74–**1.84.**
17	Cl^{+7}	**0.26.**	Cl°	1.05–1.07.	Cl^{-1}	**1.81.**
18			Ar°	(1.54).		
19	K^{+1}	**1.33**(–1.84).	K°	(2.07–)2.23.		
20	Ca^{+2}	**0.99**–1.06(–1.50).	Ca°	(1.70–)1.97.		
21	Sc^{+3}	**0.81**–0.83.	Sc°	1.51.		
22	Ti^{+4}	(0.58–)0.64–**0.68.**	Ti°	(1.40–)1.49(–1.53).		
23	V^{+5}	**0.59.**				
	V^{+4}	**0.59**–0.61.	V°	1.32(–1.43).		
24	Cr^{+6}	**0.52**–0.65.	Cr°	(1.17–)1.25(–1.54).		
25	Mn^{+7}	**0.46.**				
	Mn^{+4}	**0.50**–0.52.				
	Mn^{+2}	**0.80**–0.91.	Mn°	(1.17–)1.29(–1.59).		
26	Fe^{+3}	(0.49–)0.67.				
	Fe^{+2}	**0.75**–0.83.	Fe°	(1.21–)1.26(–1.45).		
27	Co^{+3}	0.29–0.47.				
	Co^{+2}	**0.72**–0.82.	Co°	1.26(–1.39).		
28	Ni^{+3}	0.35.				
	Ni^{+2}	**0.69**–0.78	Ni°	1.24(–1.39).		
29	Cu^{+2}	0.70.				
	Cu^{+1}	(0.58–)**0.96.**	Cu°	(1.22–)1.27(–1.37).		
30	Zn^{+2}	**0.74**–0.83.	Zn°	1.31–1.34.		
31	Ga^{+3}	**0.62.**	Ga°	(1.28–)1.33(–1.45).		
32	Ge^{+4}	0.44–**0.53.**	Ge°	1.22.	Ge^{-4}	**2.72.**
33	As^{+5}	**0.47.**				
	As^{+3}	0.69.	As°	(1.04–)1.16(–1.26).	As^{-3}	**2.22.**
34	Se^{+6}	**0.42.**	Se°	1.13–1.17.	Se^{-2}	1.91–**1.98.**
35	Br^{+7}	**0.39.**	Br°	1.19.	Br^{-1}	**1.95**–1.96.
36			Kr°	(1.69).		
37	Rb^{+1}	**1.48**–1.49(–1.88).	Rb°	(2.25–)2.36.		
38	Sr^{+2}	**1.13**–1.27(–1.45).	Sr°	1.95.		
39	Y^{+3}	**0.93**–1.06.				

40	Zr^{+4}	(0.68–)**0.80**–0.89.	Zr°	1.60–1.62.		
41	Cb^{+5}	0.69–**0.70**.				
	Cb^{+4}	**0.67**–0.69.	Cb°	1.43(–1.50).		
42	Mo^{+6}	**0.62**.				
	Mo^{+4}	**0.66**(–0.83).	Mo°	1.36.		
43	——					
44	Ru^{+4}	**0.63**–0.65.	Ru°	1.27–1.34.		
45	Rh^{+3}	0.69.	Rh°	1.34–1.35.		
46			Pd°	1.37.		
47	Ag^{+1}	(0.79–)1.13–**1.26**.	Ag°	(1.17–)1.44.		
48	Cd^{+2}	(0.78–)**0.97**–1.03.	Cd°	(1.47–)1.49(–1.60).		
49	In^{+3}	**0.81**–0.92.	In°	1.45–1.62.		
50	Sn^{+4}	(0.64–)**0.71**(–0.81).	Sn°	(1.27–)1.40.	Sn^{-4}	(2.15); **2.94**.
51	Sb^{+5}	**0.62**.				
	Sb^{+3}	0.90.	Sb°	(1.22)1.34(–1.44).	Sb^{-3}	**2.45**.
52	Te^{+6}	**0.56**.				
	Te^{+4}	**0.81**–0.89	Te°	1.33–1.43.	Te^{-2}	2.03–**2.21**.
53	I^{+7}	**0.50**.				
	I^{+5}	0.94.	I°	1.36–1.40.	I^{-1}	**2.16**–2.20.
54			Xe°	(1.90).		
55	Cs^{+1}	1.65–**1.69**(–1.75).	Cs°	(2.37–)2.55.		
56	Ba^{+2}	**1.35**–1.43(–1.49).	Ba°	2.10.		
57	La^{+3}	**1.15**–1.22.				
58	Ce^{+4}	**1.01**–1.02.				
	Ce^{+3}	1.18.	Ce°	1.82–1.83.		
59	Pr^{+4}	**0.92**–1.00.				
	Pr^{+3}	1.16.				
60	Nd^{+3}	1.15.				
61	——					
62	Sm^{+3}	1.13.				
63	Eu^{+3}	1.13.				
64	Gd^{+3}	1.11.				
65	Tb^{+3}	1.09.				
66	Dy^{+3}	1.07.				
67	Ho^{+3}	1.05.				
68	Er^{+3}	1.04.				
69	Tm^{+3}	1.04.				
70	Yb^{+3}	1.00.				
71	——					
72			Hf°	1.66.		
73			Ta°	1.42–1.44.		
74	W^{+6}	0.88.				
	W^{+4}	**0.66**–0.68.	W°	1.37.		
75	——					
76	Os^{+4}	**0.65**–0.67.	Os°	1.30–1.34.		
77	Ir^{+4}	**0.64**.–0.66.	Ir°	1.35.		
78			Pt°	1.38(–1.43).		
79	Au^{+1}	**1.37**.	Au°	1.40–1.44.		

80	Hg^{+2}	1.10–1.12.	Hg°	1.46–1.49.		
81	Tl^{+3}	0.95–1.05.				
	Tl^{+1}	1.44–1.51.	Tl°	(1.71–)1.99(–2.25).		
82	Pb^{+4}	0.84.				
	Pb^{+2}	(0.98–)1.21–1.32.	Pb°	1.74(–1.90).	Pb^{-4}	2.15.
83	Bi^{+5}	0.74.	Bi°	(1.34–)1.46(1.55).		
84 to 89	——					
90	Th^{+4}	1.02–1.10.	Th°	1.80–1.82.		
91	——					
92	U^{+4}	0.97–1.05.				
—	NH_4^{+1}	1.42–1.59.				

THE CRYSTAL FORMS OF CALCIUM SULPHATE

L. S. Ramsdell* and E. P. Partridge.**

Abstract

This paper reviews the work leading up to the statement by Linck and Jung that only three crystal forms of calcium sulphate exist. It describes some new X-ray analyses of gypsum dehydrated to less than 0.3 per cent H_2O which show that this material, commonly called "soluble anhydrite," has a crystal structure identical with that of the hemihydrate, and supports the hypothesis of Linck and Jung that the hemihydrate is zeolitic in nature, losing and regaining its water of hydration without change in crystal structure.

An equilibrium system for the three forms of calcium sulphate in contact with water is described, and some original experiments are recorded which show that gypsum is converted into anhydrite when in contact with water at 100°C, probably passing through the hemihydrate as an intermediate stage. Similar experiments conducted with anhydrite in contact with water at 11°–15°C show that it is slowly converted into gypsum. Photomicrographs of both transitions are included.

Important Researches on Calcium Sulphate

Until recently it was the generally accepted view that there were four crystal forms of calcium sulphate: gypsum, hemihydrate, "soluble anhydrite," and anhydrite. An extensive and exceedingly contradictory literature has developed concerning the relations between these various forms. The confusion of experimental data is largely the result of three factors: (1) Much of the work reported gives the results from technical investigations concerned less with the production of fundamental data than with the determination of optimum methods for plaster manufacture; (2) There has been a very general failure to differentiate between the concepts of *rate of reaction* and *equilibrium*, short-time tests of a few hours, or even of less than an hour, being accepted as conclusive data on final states; (3) There has been a frequent neglect of the influence of vapor pressure upon the changes between the various forms.

Out of the large number of investigations reported there is an important sequence of researches which lead up to the conclusion that only three crystal forms of calcium sulphate exist, rather than four, and that the material obtained by complete dehydration of gypsum at low temperatures, commonly referred to as "soluble anhydrite" is not a separate form, but has a crystal structure identical with that of hemihydrate. This sequence of researches will be briefly listed. Many of the less significant articles containing contributory evidence have necessarily been neglected in giving the general outline.

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The hemihydrate was first discovered by Millon (1). Its preparation and properties were extensively investigated by Le Chatelier (2). Both of these investigators found that the hemihydrate lost its water of hydration completely on heating, but Potilitzin (3) was the first to announce that the anhydrous calcium sulphate prepared by complete dehydration of gypsum at temperatures below 200°C. differed greatly from natural anhydrite in its properties. Lacroix (4) studied this difference crystallographically, and noted that the refractive index and double refraction of the material obtained by the dehydration of gypsum at low temperatures were decidedly lower than those of natural anhydrite. He noted the significant fact that anhydrous calcium sulphate prepared at low temperatures was oriented with respect to the original gypsum crystals, while anhydrite prepared by dead-burning gypsum was not oriented at all.

The existence of four forms of calcium sulphate was accepted by van't Hoff and his students (5), who studied extensively the equilibria between these forms in contact with water, obtaining the following transition temperatures:

Transition	Equilibrium Temperature, °C
Gypsum—anhydrite	63.5–66
Gypsum—"soluble anhydrite"	93
Gypsum—hemihydrate	107

The term "soluble anhydrite" was originated by van't Hoff to define the anhydrous form prepared from gypsum at low temperatures. Davis (6) emphasized the extremely rapid rehydration of "soluble anhydrite" in contact with moist air, and criticized van't Hoff's work on this material. Davis further stated that the dehydration of gypsum always took place through the following reversible steps:

$$\text{Gypsum} \rightleftarrows \text{Hemihydrate} \rightleftarrows \text{Soluble Anhydrite}$$

and said that hemihydrate and "soluble anhydrite" were both orthorhombic in form. Glasenapp (7), and later Gaudefroy (8), studied the dehydration of the hemihydrate crystallographically and found no change in crystal form. Gaudefroy emphasized the rapid reversibility of the change between "soluble anhydrite" and hemihydrate, and calculated from density measurements that the molecular volumes of the two forms were identical. Grengg (9) made an extended crystallographic study which confirmed the close relation of these two forms.

As the logical outgrowth of the preceding investigations, Linck and Jung (10) proposed in 1924 that "soluble anhydrite" was nothing more than hemihydrate which had zeolitically lost its water of hydration. Their heating curves and eudiotensimeter measurements show a transition of gypsum to hemihydrate at 99°C. followed by a continuous loss of water over the range 120° – 190°C. Jung (11) followed up this work by an X-ray analysis of the different forms of calcium sulphate and found but three diffraction patterns. The first was given by gypsum; the second by hemihydrate, by gypsum dehydrated to 1.5 per cent H_2O, and by commercial plaster; the third by gypsum dead-burned at a low red heat, and by natural anhydrite. This work indicated the probable identity of crystal structure of hemihydrate and "soluble anhydrite." Molecular volumes for these two materials calculated by Biltz (12) from the density measurements of Linck and Jung were identical and varied only slightly from the figures of Gaudefroy.

Jolibois and Chassevent (13) (17) have since found that solubilities determined with "soluble anhydrite" give values practically identical with those of hemihydrate. Balarew (14) has been the only one to date to attack the viewpoint expressed by Linck and Jung that there are only three true forms of calcium sulphate. His data should be extended further to be conclusive. To the present writers the hypotheses of three true crystal forms, and of the zeolitic character of hemihydrate represent more accurately the general trend of experimental observations than the hypothesis of four distinct crystal forms. It seemed, however, that the X-ray analysis of Jung based on gypsum dehydrated to a water content of 1.5 per cent should be repeated with more completely dehydrated material, with careful provision against possible rehydration during any part of the process. Some original work was, therefore, carried out which will subsequently be described.

THE DEHYDRATION OF GYPSUM IN CONTACT WITH AIR

It has been previously stated that much conflict in experimental data on dehydration is due to neglect of the effect of vapor pressure. When a hydrate, such as gypsum, is heated in air, it will lose water if the vapor pressure of the hydrate exceeds the partial pressure of the water vapor in the air in contact with it. Hannay (15) emphasized this fact with reference to the dehydration of gypsum in 1877, but it has repeatedly been ignored, even since van't Hoff's measurements of the vapor pressure of calcium sulphate systems as a function of temperature. Under ordinary conditions of experimentation the air is not saturated with water vapor, and the temperature at which dehydration takes place will depend upon the partial pressure of the water vapor in the air. By lowering the partial pressure of water vapor in the air, it is possible to lower the temperature at which dehydration will take place. Thus Shenstone and Cundall (16), and van't Hoff and his students both obtained complete dehydration of gypsum at 70°C. when in contact with air dried over phosphorus pentoxide, and Jolibois (17) states that complete dehydration may be obtained at room temperatures with air dried in this manner, several weeks, however, being required. The lowest possible temperature at which dehydration will occur is indeterminate, for decreasing the temperature decreases the vapor pressure of the hydrate and the time factor becomes indefinitely large because of the small driving force for the reaction.

In the experimental work of the authors it was only desired to obtain complete dehydration of gypsum for the purpose of obtaining samples of "soluble anhydrite" for X-ray analysis. No study of dehydration rates or limiting temperatures was intended. At the temperatures used in these experiments, the vapor pressure of the hydrate was always at least 100 times the partial pressure of the water vapor in the atmosphere, and the time allowed for dehydration varied from one to five days. The material used was either pure selenite gypsum powdered to pass 200-mesh, or a pure precipitated gypsum (Baker's Analyzed C. P.).

The results of the dehydration experiments are expressed for convenience in three series. Series A constituted a check on the dehydration of the materials used, and was carried out in open weighing bottles heated in an electric oven at different temperatures for different periods. The bottles were closed while hot and cooled in a desiccator.

Series B provided the material for the X-ray analysis of "soluble anhydrite." The sample of gypsum was placed in a special tube drawn to a capillary at one end and sealed, and fitted at the other end with a ground glass stopper. The tube was first weighed by itself and again after introduction of a sample of gypsum into the large part. The open tube was heated at the temperatures and for the periods indicated, using an electric oven, and the stopper was then inserted, the tube cooled in a desiccator, and the loss of water determined. Some of the powder was then shaken down into the capillary, which was sealed off and used for X-ray determinations of crystal structure. By this procedure any rehydration of the material during handling was obviated, and a sample of "soluble anhydrite" containing not more than 0.3 per cent of water was obtained.

Series A and B were both carried out in contact with the laboratory atmosphere. A check on Series B was desired with material prepared in a stream of dry air. In this work, which will be referred to as Series C, an air drying train utilizing first $CaCl_2$ and then P_2O_5 was used, and no attempt was made to determine the loss of weight of the sample, since the results of Series B indicated that practically complete dehydration was attained at the temperatures used, within the period of the experiment.

Table 1. The Dehydration of Gypsum in Air

	Temperature °C	Duration of heating-hrs.	Weight of sample gr.	Loss in weight gr.	Loss in weight %
Series A	120	20	1.5391	0.3143	20.42
	120	68	1.5391	0.3145	20.43
	120	68	1.5795	0.3236	20.48
	143	17	3.0037	0.6007	20.00
	143	60	3.3437	0.6663	19.93
	143	60	2.4479	0.4871	19.90
	150	72	1.8943	0.3820	20.16
	150	72	1.9838	0.4000	20.16
Series B	150	120	0.2484	0.0512	20.61
	150	120	0.2382	0.0493	20.70
	180	48	0.3633	0.0741	20.39
	180	120	0.4127	0.0847	20.52

Series C	150	48	—	—	—
	180	48	—	—	—
Average % loss for all determinations					20.31
Theoretical loss for complete dehydration					20.93

The practically anhydrous product secured in the above experiments was distinct from anhydrite, or from dead-burned gypsum, both in its optical properties and in its X-ray diffraction pattern. The patterns found for the samples from Series B and C, carefully guarded from any possible rehydration, were identical with those obtained from material from Series A, which had been allowed to partially rehydrate in contact with the laboratory air, and were also identical with those obtained from plaster-of-Paris. It is, therefore, concluded that the identity of crystal structure of hemihydrate and "soluble anhydrite" is established.

The partial rehydration of "soluble anhydrite" to form hemihydrate was confirmed in the course of the experimental work. The two samples from Series A which had been dehydrated at 150°C. were used, one of them being left covered as a check, and the other being exposed to the air of the laboratory. The gain in weight of the latter sample is indicated in Table 2. The partial pressure of water vapor in the air was approximately equal to the equilibrium vapor pressure for the hemihydrate-gypsum transition.

TABLE 2. REHYDRATION OF COMPLETELY DEHYDRATED GYPSUM

Weight of Original Gypsum Sample gr.	Loss in Weight on Dehydration %	Duration of Rehydration days	Weight of Sample gr.	Gain in Weight %
Exposed to Air				
1.9838	20.16	1	1.6348	2.57
		2	1.6943	5.57
		4	1.6979	5.75
		7	1.6962	5.66
		9	1.6943	5.57
Not Exposed to Air				
1.8943	20.16	1	1.5128	0.03
		2	1.5140	0.11
		3	1.5152	0.16
		4	1.5188	0.40
Theoretical gain to form hemihydrate				5.24

During the dehydration experiments there was no suggestion of the formation of any intermediate product, such as the hemihydrate, which would have a theoretical loss of 15.69 per cent of the original gypsum. This is to be expected at the temperatures used, since the partial pressure of water vapor in the air is far below the vapor pressure of the hemihydrate as well as that of gypsum. The dehydration reaction therefore consists of two simultaneous reactions:

$$CaSO_4 \cdot 2H_2O \rightleftarrows CaSO_4 \cdot \tfrac{1}{2}H_2O + \tfrac{3}{2}H_2O$$

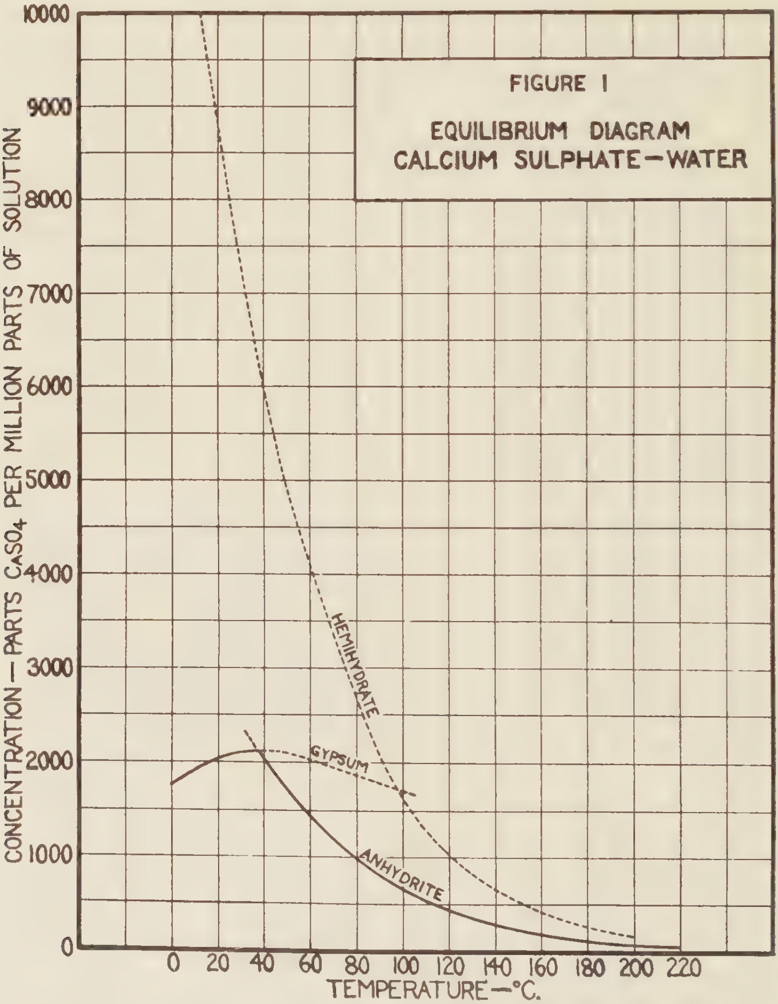
$$CaSO_4 \cdot \tfrac{1}{2}H_2O \rightleftarrows CaSO_4(\text{``soluble anhydrite''}) + \tfrac{1}{2}H_2O$$

As soon as the hemihydrate is formed, it begins to lose water, and equilibrium is reached only when the vapor pressure of the zeolitic water of hydration of the hemihydrate is equal to the partial pressure of the water vapor in the atmosphere. It should be noted at this point that if the zeolitic nature of the hemihydrate is accepted, it is theoretically impossible to obtain absolutely complete dehydration in contact with an atmosphere containing any water vapor. This would account for the consistent failure of dehydration data to attain to the theoretical per cent loss of 20.93 for the complete dehydration of pure gypsum.

In view of the vapor pressure considerations noted above, the conclusions of Parsons (18) that plaster-of-Paris is not a definite chemical compound, and that gypsum loses all of its water of crystallization in a single stage are not tenable. Jolibois (17) has prepared hemihydrate by heating gypsum to 140°C. in a covered crucible. In this way the water of hydration lost from the gypsum raised the partial pressure of the water vapor in the air within the crucible to the degree necessary to stop the dehydration at the end of the first reaction given above.

THE EQUILIBRIUM SYSTEM FOR THE THREE CRYSTAL FORMS OF CALCIUM SULPHATE IN CONTACT WITH WATER

The foregoing work presents strong evidence of the existence of only three crystal forms of calcium sulphate. If, however, hemihydrate and "soluble anhydrite" are to be considered identical, a revision of the equilibrium diagram for the forms of calcium sulphate in contact with water is necessary. Such a revised diagram has been proposed by Partridge and White (19) as the result of a re-determination of solubility values for calcium sulphate above 100°C. This equilibrium diagram, shown in Figure 1, is based upon the data of a number of investigators. The excellently concordant values of Raupenstrauch (20a), Hulett and Allen (20b), Melcher (20c), and Cavazzi (20d), have been used to determine the curve for gypsum. It was found that the solubility curve for hemihydrate below 100°C. determined by Chassevent



(20e) was continuous with the curve above 100°C. originally determined by Boyer-Guillon (20f), and commonly referred to as the curve for "soluble anhydrite." Partridge and White re-determined this latter curve and found by optical and X-ray methods that the solid phase was hemihydrate. The curve for anhydrite is based on the data of Melcher, the minimum values of Hall, Robb, and Coleman (20g), and the data of Partridge and White, for its course above 100°C. Below this temperature there is but one determination available in the literature, that of Haddon and Brown (20h) at 33°C. The curve determined above 100°C. has been extended to pass through this point.

From the curves of Figure 1 the following transition temperatures between the forms of calcium sulphate in contact with water are obtained:

Transition	Equilibrium Temperature °C
Gypsum—anhydrite	38
Gypsum—hemihydrate	98

The hemihydrate curve shows no intersection with the anhydrite curve in the range from 0° to 200°C.

The transition temperature of 38°C. for the change from gypsum to anhydrite in contact with water can only be considered as provisional until extended and accurate measurements of the solubility of anhydrite are made in the range from 0° to 100°C. This provisional transition temperature is appreciably lower than that of 63.5–66°C. given by van't Hoff.

Apparent Anomalies in the Equilibrium Diagram for Calcium Sulphate and Water

On inspection of Figure 1, it appears that gypsum should be the stable solid phase in contact with water below a temperature of 38°C. and that anhydrite should be the stable solid phase in contact with water above that temperature, while hemihydrate should exist only as an unstable solid phase in contact with water at all temperatures over the range from 0° to 200°C. This general statement is partially contradictory to common experience, for gypsum presents apparent stability in contact with water up to its transition into hemihydrate at 98°C. instead of being transformed into anhydrite at a much lower temperature. This apparent stability of gypsum requires further long-time study. Work is in progress by the authors on this question.

The general statement given above is in accord with common experience concerning the instability of hemihydrate. Hemihydrate has never been reported in a natural occurrence with the exception of one possible case noted by Sworykin (21). In contact with water below 98°C. it rehydrates to form gypsum, while in contact with water above this point it changes gradually to anhydrite.

From the equilibrium diagram it is evident that between 38° and 98°C. gypsum in contact with water should change into anhydrite without passing through the intermediate stage of the hemihydrate, while below 38°C. hemihydrate in contact with water should change into gypsum through anhydrite as an intermediate stage. Further work is necessary to clear up these unusual relations implied by the course of the solubility curves.

The relative stability of gypsum and anhydrite above 98° and below 38°C. has been tested by the authors in some original work which will be described in the following section.

The Dehydration of Gypsum and Rehydration of Anhydrite in Contact with Water

Davis (6) has stated that minute gypsum crystals are converted into hemihydrate within a few hours when in contact with water at the atmospheric boiling point, and Farnsworth (22) has observed a slower transition of gypsum to hemihydrate in contact with water at 110°C. These observations are in accord with the equilibrium diagram of Figure 1, since at 100°C. gypsum represents a solid phase unstable with respect to hemihydrate. Hemihydrate, however, is also unstable with respect to anhydrite, and it would be expected that gypsum should ultimately be replaced by anhydrite, with hemihydrate as an intermediate stage.

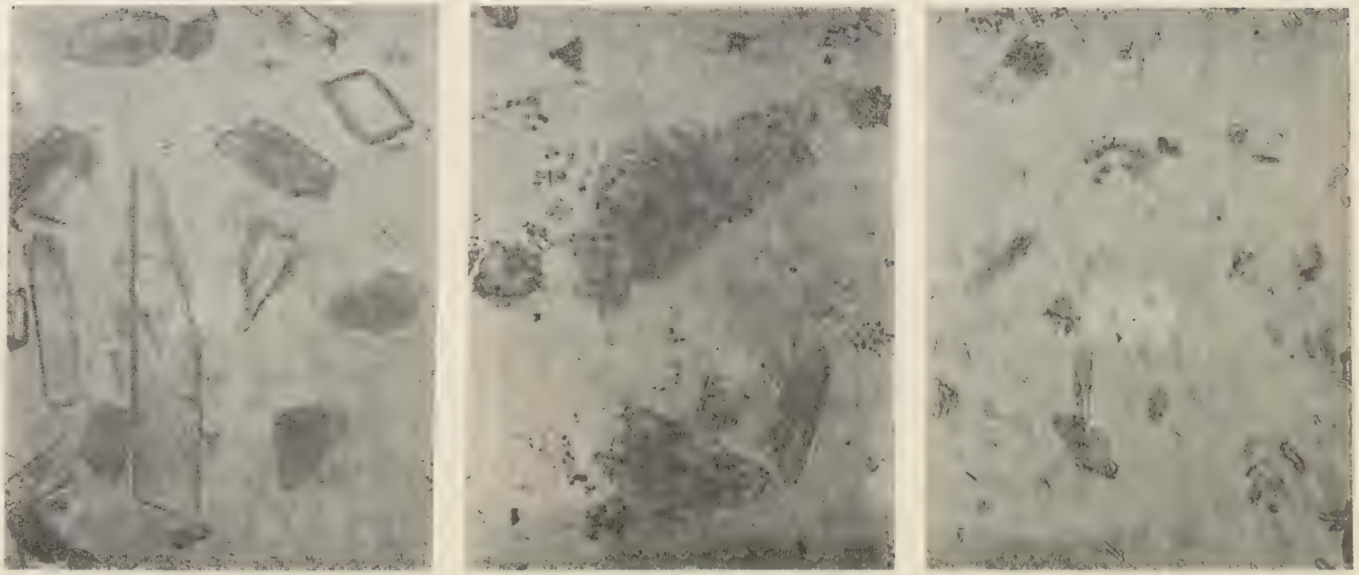
The change of anhydrite to gypsum when in contact with water at ordinary atmospheric temperatures is a well-known geological phenomenon, and has been noted in the laboratory by Gill (45)(23), but only after an extremely long period. Both this change, and that from gypsum to hemihydrate at 100°C. are analogous to the setting of plaster-of-Paris in that a more soluble form goes into solution with subsequent recrystallization of a less soluble form.

Some original experiments were made by the authors at 100°C. and at 11°–15°C. to determine accurately the dehydration of gypsum at the former temperature and the rehydration of anhydrite at the latter temperature. These will be referred to, respectively, as Series D and Series E.

For the experiments of Series D a pure sample of selenite gypsum was powdered and screened, and the portion which passed a 100-mesh screen and was retained on a 150-mesh screen was used. Samples of this material of approximately 0.2 gram each were placed in small test tubes with 5 cc. of distilled water. The tubes were heated to 100°C. in a water bath and were sealed off and then were suspended in distilled water boiling under atmospheric pressure. After various periods of time, tubes were removed and the contents were immediately filtered and washed with alcohol and with ether on a suction filter, after which they were examined optically.

The original material consisted chiefly of clear angular cleavage fragments, with low double refraction and inclined extinction. Some of the grains seemed to have been shattered by the powdering and appeared as fine-grained aggregates. After ten days in contact with water at 100°C a sample was examined and it was found that the shattered gypsum grains had disappeared and the cleavage fragments were distinctly corroded. A sample taken after twenty days showed further disintegration of the gypsum. In both of these samples there appeared a new product which consisted essentially of radiating clusters of very minute doubly refracting prisms embedded in an isotropic material. No satisfactory identification of this material could be made by optical methods, and the X-ray results were likewise inconclusive. Due to the small change between the 10-day and 20-day samples, the next sample was not taken until 46 days had elapsed. In this sample the gypsum had entirely disappeared, the intermediate phase had partially disappeared, and a large number of rectangular crystals of anhydrite had appeared. These gave the characteristic refractive indices, high double refraction, and parallel extinction of anhydrite and this determination was checked by X-ray analysis which gave the characteristic diffraction pattern for this form of calcium sulphate. The earlier samples showed only the characteristic lines of gypsum on X-ray analysis. Judging from the solubility curves, and from the work of Davis and of Farnsworth, hemihydrate would be expected as an intermediate product. This was not proved in the present experiment. The intermediate phase described above may have been hemihydrate, but the amount in any one sample was insufficient to produce an X-ray pattern. Figure 2 shows photomicrographs of the original gypsum, the intermediate phase, and the new crystals of anhydrite.

Fig. 2.—The Conversion of Gypsum to Anhydrite in Contact with Water at 100°C.



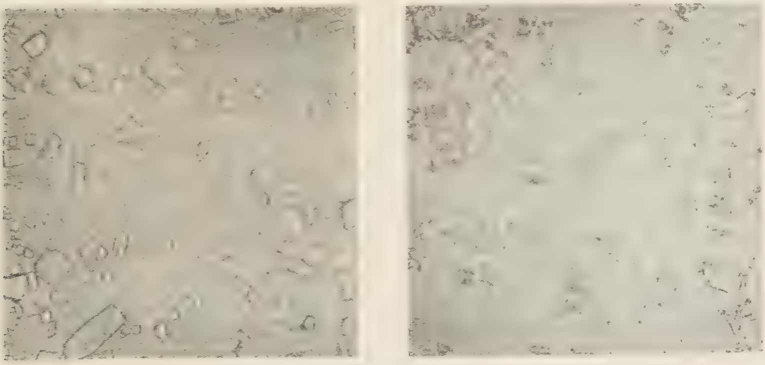
A
Original Gypsum Fragments. ×70.

B
Intermediate Phase and Corroded Gypsum Fragments after 10 days in water at 100°C. ×90.

C
Anhydrite and Residual Intermediate Phase after 46 days in water at 100°C. ×70.

For the experiments of Series E powdered anhydrite and dead-burned gypsum were used. Several samples of each were sealed in glass tubes containing distilled water, and these tubes were held between 11° and 15°C. in a water bath. After 45 days the dead-burned gypsum had entirely disappeared and was replaced by gypsum crystals, of a short prismatic type and untwinned. The natural anhydrite changed much more slowly, and after 120 days still showed a few unchanged grains of anhydrite. The greater portion, however, was in the form of small gypsum crystals, either short untwinned prisms, or needles showing the characteristic swallow-tail twinning. Figure 3 shows photomicrographs of the original anhydrite used in this experiment and of the product after 120 days contact with water at 11°–15°C.

FIG. 3.—The Conversion of Anhydrite to Gypsum in Contact with Water at 11°–15°C.



A
Original Anhydrite Fragments. ×95.

B
Gypsum Crystals and Residual Anhydrite Fragments after 120 days in water at 11°–15°C. ×95.

A third series of experiments at a temperature of 50°C. is still in progress. Gypsum was used as the initial solid phase in tubes containing water as before. These were sealed off at 50°C. and were maintained at that temperature in an electric oven. After 120 days there was no evidence of any change. The crystals showed no sign of solution, and there was no new product formed. This either indicates that gypsum is less soluble than anhydrite at this temperature and is therefore the stable phase, and that therefore the intersection of the solubility curves for gypsum and anhydrite should lie above 50°C., or else it indicates that this temperature is so near the point of intersection that the rate of reaction is extremely slow. This experiment cannot be regarded as furnishing any definite information at the present time and is being continued.

The analogy of the solution of plaster-of-Paris with subsequent recrystallization of gypsum to the change from gypsum to anhydrite at 100°C. and the change from anhydrite to gypsum at 11°–15°C. is emphasized by the fact that in both of the series of experiments a distinct setting of the samples was observed. On the other hand, a sample of hemihydrate added to water maintained at 100°C. did not set at all during a period of three days. This was to be expected, since the hemihydrate is less soluble than gypsum at 100°C. and therefore would not be expected to rehydrate, while the conversion to anhydrite is such a slow reaction that no setting from this cause was apparent during the time of the experiment.

Conclusions

(1) Three crystal forms of calcium sulphate exist, rather than four. These are gypsum, hemihydrate, and anhydrite. "Soluble anhydrite" is identical in crystal structure with hemihydrate, the latter apparently belonging to the zeolitic class of substances which lose and regain water of hydration without change in crystal structure. The term "hemihydrate" should, therefore, be interpreted not as referring to a compound with a definite water content, but as referring to a compound which gives a certain definite X-ray diffraction pattern. The term "soluble anhydrite" is a misnomer, and should be replaced by the term "dehydrated hemihydrate" which more nearly expresses the true relationship of the hemihydrate and the material obtained by complete dehydration at low temperatures.

(2) The transition temperature for the change from gypsum to anhydrite when in contact with water is provisionally placed at 38°C.; for the change from gypsum to hemihydrate, when in contact with water, is more definitely placed at 98°C.

(3) Anhydrite has been obtained experimentally from gypsum in contact with water at 100°C., with evidence of setting similar to that of plaster-of-Paris.

(4) Gypsum has been obtained from anhydrite in contact with water at 11°–15°C., with evidence of setting similar to that of plaster-of-Paris.

(5) The conversion of gypsum to anhydrite at 100°C. and of anhydrite to gypsum at 11°–15°C. are analogous to the conversion of hemihydrate to gypsum noted in the setting of plaster. In each case a more soluble unstable solid phase dissolves in water, with subsequent crystallization of a less soluble stable phase from the solution which is supersaturated with respect to it.

References

(1) Millon, E. Remarks on Some Examples of Chemical Affinity, *Ann. Chim. Phys.*, (3) **19**, 222–230 (1847).

(2) Le Chatelier, H. Experimental Researches on the Constitution of Hydraulic Mortars. *Paris* (**1887**); Concerning the Setting of Plaster, *Compt. Rend.*, **96**, 1668–1671 (1883).

(3) Potilitzin, A. Concerning the Solubility of Anhydrous Gypsum, *J. Russ. Phys. Chem. Ges.*, **26**, 170 (1894); **26**, 221–229 (1894); **27**, 265–270 (1895); *Berichte*, **27** (4), 613–616 (1894); *Chem. Zentr.*, (**1894**), 515, 609.

(4) Lacroix, A. On Anhydrous Calcium Sulphate Produced by the Complete Dehydration of Gypsum, *Compt. Rend.*, **126**, 360–362 (1898).

On the Formation of Anhydrite by the Calcination of Gypsum at a High Temperature, *Compt. Rend.*, **126**, 553–554 (1898).

(5) van't Hoff, J. H.; Armstrong, E. F.; Hinrichsen, W.; Weigert, F.; Just, G. Gypsum and Anhydrite, *Z. Phys. Chem.*, **45**, 257–306 (1903).

van't Hoff, J. H.; Hinrichsen, W.; Weigert, F. *Sitzber. Akad., Berlin* (**1901**) 570.

van't Hoff, J. H.; Weigert, F. *Sitzber. Akad., Berlin* (**1901**) 1140.

van't Hoff, J. H.; Armstrong, E. F. *Sitzber. Akad., Berlin* (**1900**) 563.

van't Hoff, J. H.; Just, G. *Sitzber. Akad., Berlin* (**1903**) 249.

(6) Davis, W. A. The Nature of the Changes Involved in the Production and Setting of Plaster-of-Paris, *J. Soc. Chem. Ind.*, **26**, 727–738 (1907).

(7) Glasenapp, M. Studies on Plaster of Paris, Dead-Burned Gypsum, and Estrichgyps. *Tonind. Z.*, **32**, 1148–1152 (1908).

(8) Gaudefroy, C. On the Dehydration of Gypsum, *Compt. Rend.*, **158**, 2006–2007 (1914); **159**, 263–264 (1914).

(9) Grengg, R. The Dehydration Products of Gypsum, *Z. Anorg. Chem.*, **90**, 327–360 (1914).

(10) Linck, G., and Jung, H. Concerning the Dehydration and Rehydration of Gypsum, *Z. Anorg. Allgem. Chem.*, **137**, 407–417 (1924).

(11) Jung, H. X-Ray Investigations of the Dehydration Products of Gypsum, *Z. Anorg. Allgem. Chem.*, **142**, 73–79 (1925).

(12) Biltz, W. Note Concerning the Volume of Water in the Hydrates of Calcium Sulphate. *Z. Anorg. Chem.*, **143**, 231–232 (1925).

(13) Jolibois, P., and Chassevent, L. On the Setting of Plaster, *Compt. Rend.*, **177**, 113–116 (1923).

(14) Balarew, D. Concerning the Dehydration of Gypsum, *Z. Anorg. Chem.*, **156**, 258–260 (1926).

Concerning the Equilibrium between the Hydrates of Calcium Sulphate. *Z. Anorg. Chem.*, **163**, 137–140 (1927).

(15) Hannay, J. B. Examination of Substances by the Time Method, *J. Chem. Soc.*, **32**, 381–395 (1877).

(16) Shenstone, W. A., and Cundall, J. T. The Influence of Temperature on the Composition and Solubility of Hydrated Calcium Sulphate and of Calcium Hydroxide, *J. Chem. Soc.*, **53**, 544–550 (1888).

(17) Jolibois, P. Plaster, *Bull. Soc. Chim.*, **41**, 117–135 (1927).

(18) Parsons, A. L. *Contributions to Canadian Mineralogy*, **1927**, *University of Toronto Studies No.* **24**, pp. 24–27.

(19) Partridge, E. P., and White, A. H. The Solubility of Calcium Sulphate from 0° to 200°C. *J. Am. Chem. Soc.*, **51**, —— (1929). (Not yet published at time of printing).

(20a) Raupenstrauch, G. A. Concerning the Measurement of the Solubility of Some Salts in Water at Different Temperatures, *Monatshefte für Chemie*, **6**, 563–591 (1885).

(20b) Hulett, G. A., and Allen, L. E. The Solubility of Gypsum, *J. Am. Chem. Soc.*, **24**, 667–669 (1902).

(20c) Melcher, A. C. The Solubility of Silver Chloride, Barium Sulphate, and Calcium Sulphate at High Temperatures, *J. Am. Chem. Soc.*, **32**, 50–66 (1908).

(20d) Cavazzi, A. The Solubility, Supersaturation, and Setting of Gypsum, *L'Industria Chimica*, **6**, 366–368 (1904); *Chem. Zentr.*, (5) **9**, 1693–1694 (1905).

(20e) Chassevent, L. Researches on Calcium Sulphate. I. Action of Water on Calcium Sulphate, *Ann. Chim.*, (10) **6**, 244–294 (1926).

Researches on Plaster, *Bull. Soc. Encour. Ind. Nat.*, 789–803, (**1926**).

(20f) Boyer-Guillon, A. Study of the Solubility of Calcium Sulphate, *Ann. Conserv. Arts et Metiers*, (3) **2**, 187–211 (1900).

(20g) Hall, R. E.; Robb, J. A., and Coleman, C. E. The Solubility of Calcium Sulphate at Boiler-Water Temperatures, *J. Am. Chem. Soc.*, **48**, 927–938 (1926).

(20h) Haddon, C. L., and Brown, M. A. W. Calcium Sulphate Cement, *J. Soc. Chem. Ind.*, **43**, 11–16T (1924).

(21) Sworykin, A. J. Concerning the Question of the Solubility of the Natural Hemihydrate of Gypsum after its Heating at Different Temperatures, *Z. Anorg. Chem.*, **163**, 178–184 (1927).

(22) Farnsworth, M. The Hydration of Anhydrite, *Ind. Eng. Chem.*, **17**, 967–970 (1925).

(23) Gill, A. C. The Hydration of Anhydrite and Dead-Burned Gypsum, *J. Am. Ceram. Soc.*, **1**, 65–71 (1918).

NOTES AND NEWS

MANGANOTANTALITE FROM PORTLAND, CONNECTICUT

W. G. Foye, *Middletown, Conn.*

On October 2nd the writer visited the Collins Hill Quarry, Portland, Connecticut, with a class in geology. Mr. Wilkes, who now operates the quarry, asked him to identify a new mineral which he had found. The writer was unable to recognize the mineral and Mr. Wilkes kindly gave it to him for further investigation.

The mineral was imbedded in orthoclase feldspar near a larger crystal of columbite. It was reddish brown in color and showed two cleavages at right angles; one cleavage was fairly perfect and the second was much less perfect. The rectangular outlines of the crystal indicated that it was probably orthorhombic in crystal form. Its hardness was about 5.

The mineral gave a strong reaction for manganese in a soda bead but was infusible and insoluble. Tests for the commoner acid radicals were negative.

Optical tests showed that it was pleochroic in reddish brown to yellow; was biaxial and optically positive. As the writer had no liquids in his laboratory sufficiently high to determine the index of refraction of the mineral, he gave it to Professor Esper S. Larsen, Jr., of Harvard University for further optical tests.

Professor Larsen reported that the refractive indices were as follows: $\alpha=2.15$, $\beta=2.17$, $\gamma=2.25$, approximately. The angle 2V was medium in value and $\rho<\nu$ strong.

The mineral is probably manganotantalite, high in tantalum. It adds a new mineral to the list of twenty-seven already reported from the Collins Hill Quarry.

LARGE TOPAZ CRYSTAL FROM MAINE

W. D. Nevel, *Andover, Maine.*

From the region known as Mt. Apatite in the town of Auburn, Maine, there have been found in times past minerals of rare beauty and considerable value. From there came the rich crystals of purple apatite closely resembling in color those royal amethysts of Siberia. Tourmalines possessing the much coveted shade of blue-green were also found there and about that time a huge cavity of cavern-like proportions was opened that contained many fine, large crystals of deep smoky quartz. These glossy crystals were in many cases attached to the planes of pure white quartz making a pleasing contrast. This find helped substantially in making the locality popular with mineral collectors.

Forty-three and three-fourths carats is the weight of what is undoubtedly the largest blue topaz gem from New England or any locality east of Texas. The crystal that produced it was found in a tourmaline cavity at Mt. Apatite many years ago by Mr. John Seaver Towne who operated there for tourmaline and feldspar. Later it was sold to Mr. L. B. Merrill of Paris, Maine, who was at that time operating at Mt. Mica for tourmaline and in whose possession it remained in its crystal state about twenty years when, in 1928, having been again purchased it was turned over to a New York lapidary and beautifully cut in the cushion style yielding a perfect stone with vivid reflections of pale blue. Late in that year it was acquired by the U. S. National Museum of Washington for their gem collection.

Dr. Karl Hermann Scheumann of Berlin has been called to a professorship of mineralogy and petrography at the University of Leipzig.

Readers of The American Mineralogist are urged to submit scientific articles and notes of mineralogical interest to the Editor for publication in the Journal. More material is necessary if the Journal is to appear regularly and maintain its present size.

REVIEWS

ANLEITUNG ZUR CHEMISCHEN GESTEINSANALYSE. J. Jakob. VII+81 pages with 3 illustrations. Gebrueder Borntraeger, *Berlin*, 1928. Price 7 R. M.

This "Büchlein" attempts to instruct the student within the compass of 79 pages in the making of the chemical analysis of rocks, by which igneous ones are mostly meant. The student is assumed to have some knowledge of general quantitative analytical procedure or to work under the supervision of an instructor. The methods, in general, follow those of Hillebrand and of the reviewer, but there are many complexities and variations in the details, and some of these differences are wide and unexpected. Some of the descriptions are ultra-detailed, while in other cases an important determination is treated with unsatisfactory brevity. One page, for instance, is devoted to the method for determining the amount of FeO, while two pages are given to that for Li_2O. The reviewer differs with the author as to many particulars, such as: the possible use of porcelain crucibles for the Na_2CO_3 fusion; the advocacy of the old and very inaccurate Cooke method for FeO instead of the rapid and accurate Pratt method; the use of H_2SO_4 instead of HCl in several processes; the inordinate quantities of hydrofluoric acid that are recommended; the non-use of molten pyrosulphate for bringing the Al_2O_3, etc. precipitate into solution; and the details of many other procedures too numerous to be mentioned here. The author advocates the determination of several constituents in aliquot parts of a filtrate, whereby the accuracy is impaired. This is, also, unnecessary as the amount of the rock-powder is, or should be, sufficient to make some of the author's material-saving procedures uncalled for, although they may be advisable or necessary in the analysis of a mineral when the amount of material available may be only one or two grams. Much stress is placed on accuracy, but the attainment of this is, in many cases, rendered difficult by the elaborate and complicated precautions that are taken to ensure it. The book, on the whole, is distinctly disappointing and, for a modern textbook, does not compare favorably with the earlier ones by Dittrich and by Jannasch.

The reviewer takes this opportunity to deplore the very unsatisfactory and inadequate way in which the quantitative analysis of the silicates, including rocks and minerals, is treated in the standard manuals of quantitative analysis, such as those of Fresenius and Treadwell-Hall.

Henry S. Washington

DONNÉES NUMÉRIQUES DE CRISTALLOGRAPHIE ET DE MINÉRALOGIE. L. J. Spencer. VIII+56 pages. Price bound 50 Fr. A section of VOL. VI of the TABLES ANNUELLES DE CONSTANTES ET DONNÉES NUMÉRIQUES (1923–1924). Editor, M. Ch. Marie. Gauthier-Villars et Cie., 55 Quai des Grands-Augustins, *Paris;* McGraw-Hill Book Co., *New York*, **1928**.

This section of the Annual Tables contains new crystallographic and mineralogical data that appeared in 1923–1924, as recorded in 98 different publications. The various headings are: (1) Crystallography (minerals); (2) New crystalline forms of minerals; (3) Crystallography (inorganic substances); (4) Crystallography (organic substances); (5) Structure of crystals by X-rays; (6) Miscellaneous data including compressibility, thermal conductivity, heat of crystallization of mixed crystals, effect of pressure on melting point, etc.

This handy volume will be found to be indispensable to all mineralogists because of the wealth of material thus conveniently brought together from sources that, in many instances, would be difficult to consult in the original.

W. F. H.

PROCEEDINGS OF SOCIETIES

PHILADELPHIA MINERALOGICAL SOCIETY

Academy of Natural Sciences of Philadelphia, December 6, 1928.

A stated meeting of the Philadelphia Mineralogical Society was held on the above date with the president, Mr. Trudell, in the chair. Seventy persons were present, including thirty-two members.

Upon favorable recommendation by the council, Mr. Charles M. B. Cadwalader was elected a member.

Mr. James G. Manchester addressed the society on *Minerals of New York City and its Environs.* The results of thirty years of assiduous collecting within fifty miles of New York City were described and illustrated with a large series of colored lantern slides and beautiful specimens. Of particular interest were the minerals found in the excavations contiguous to Broadway, and those of the crystalline limestone of the upper end of Manhattan. The minerals of Tilly Foster; Kinkle's quarry, Bedford, N. Y.; the trap quarries of Paterson, and the Erie Cut, made the district a local collector's paradise. A rising vote of thanks was tendered to Mr. Manchester for his most interesting address.

Mr. Knabe reported finding blue quartz and garnet at Iveland Station. Mr. Strock described visits to Moore Station, the Perkiomen lead and zinc mines, and Perkiomenville, exhibiting large slabs of small heulandite crystals from the latter locality. Mr. Cienkowski described visits to Henderson, Mineral Hill, and Moore, Pa. Dr. Cajori reported finding jefferisite and clinochlore at Brinton's quarry. Mr. Biernbaum described a visit to the old Phoenixville lead mines which yield much pyromorphite suitable for microscopic mounts. Dr. Gilliland exhibited rhodonite crystals from Franklin, tourmaline from Newry, Maine, and an amethyst geode.

Dr. Newcomet described some experiments on the effect of radium emanations on smoky quartz, and the decolorization of this mineral at low temperatures.

Samuel G. Gordon, *Secretary*

NEW MINERAL NAMES

Monrepite

Walter Wahl: Die Gesteine des Wiborger Rapakiwigebietes. (The Rocks of the Wiborg rapakiwi area). *Fennia.* (*Bull. Soc. Géogr. Finlande*), **45,** No. 20, p. 87, 1925.

Name: From the locality, Monrepos, near Wiborg, Finland.

Chemical Properties: A ferro-ferri-mica $H_2K\ Fe''_3Fe'''\ (SiO_4)_3$. Analysis: (quoted from H. Struve, *Mém. Acad. Imp. Sci. St. Petersburg*, Sér. **VII**, 1863, TVI No. 4) SiO_2 32.73, TiO_2 1.93, Al_2O_3 13.49, Fe_2O_3 15.41, FeO 23.39, MnO 0.84, MgO 1.77, Na_2O 0.48, K_2O 8.73, H_2O 0.75. Sum 99.52.

Occurrence: Found as the black mica of the rapakiwi granite.

W. F. Foshag

Pseudoglaucophane

L. Duparc: Sur une amphibole du groupe de la glaucophane. (An Amphibole of the Glaucophane Group). *Compt. Rend. Soc. Phys. Hist. Nat. Geneve*, **44**, 48–49, 1927.

Crystallographic Properties: Crystals greatly elongated with (110) and rarely (010).

Optical Properties: Plane of the optic axes perpendicular to (100). Acute bisectrix = X. Y = Z of normal glaucophane. Birefringence: $\gamma-\alpha=0.014$, $\gamma-\beta=0.0015$, $\beta-\alpha=0.0115$. Pleochroism: X = pale yellow, Y = dark blue, Z = dark violet. Extinction Y on (100) = 6°. 2V = 40°.

Occurrence: Found as a zone about normal glaucophane from the Urals. Also in a glaucophane schist (locality not given).

W. F. F.

Ferrothorite

A. Lacroix: Minéralogie de Madagascar, vol. 3, pp. 309–310, **1923.**

Name: a ferriferous thorite.

Chemical Properties: SiO_2 12.6, ThO_2 61.5, U_3O_8 2.8, Fe_2O_3 13.1, H_2O+ 5.5, H_2O- 4.0; Sum 99.5.

Occurrence: As reddish brown crystals several centimeters in length at Befarita, Madagascar, associated with betafite.

W. F. F.

NEW DATA

Rhomboclase

Joseph Krenner: Zwei neue Mineralien aus Ungarn. (Two new minerals from Hungary). *Centr. Min. Geol.*, **1928.** Abt. A, No. 8, 265–268. Preliminary description: *Akademiai Értesitö.*, 2, 96, **1891.**

Name: In allusion to its rhombic form and good cleavage.

Chemical Properties: An acid sulfate of iron. $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. Analysis (by Josef Loczka): SO_3 49.27, Fe_2O_3 24.54, FeO 0.35, CuO 0.03, CaO 0.10, Mg(Na_2)O 0.15, Al tr., H_2O (by difference) 25.54. Before the blowpipe large fragments shrink together and leave a cokelike slag, small fragments fuse to a pearl gray enamel.

Crystallographic Properties: Orthorhombic. Crystals are tabular in habit. Forms: *c* (001), *p* (111), *m* (110), *b* (010), *d* (011). $a:b:c=0.56965:1:0.94644$. $m:m=58°36'$, $p:p=101°28'$. Basal cleavage good.

Physical and Optical Properties: Color, colorless to gray. Transparent to opaque. Luster vitreous to greasy. Hd = gypsum. Flexible. Biaxial, negative. Axial angle large. $2H_o=137°9'$. Plane of the optic axes parallel to (100). Birefringence fairly strong. (Larsen: The Microscopic Determination of the nonopaque Minerals gives $\alpha=1.533$, $\beta=1.555$, $\gamma=1.635$. 2V small, Z=elongation. The discrepancy between these figures and those of Krenner's lies in the fact that K. has mistaken the figure obtained on the base for that of the acute bisectrix.)

Occurrence: Found with other sulfates at the pyrite mines of Szomolnok, Hungary.

Szomolnokite

Ibid., p. 268–270.

Name: From the locality, *Szomolnok*, Hungary.

Chemical Properties: A sulfate of iron, $FeSO_4 \cdot H_2O$. Analysis (by Josef Loczka): SO_3 47.96, FeO 39.42, Fe_2O_3 1.36, CuO 1.20, CaO 0.07, MgO 0.25, $Na_2(K_2)O$ 0.31, ZnO 0.14, H_2O 10.36. Before the blowpipe it becomes black and fuses to a dull gray enamel.

Crystallographic Properties: Monoclinic. Prismatic crystals with (111), rarely small (113) and (110). $a:b:c=0.9544:1:1.8999$, $\beta=86°39'54''$. 111:111 =79°32′.

Physical and Optical Properties: Color sulfur yellow, pea yellow, hyacinth red, or light brown. Transparent to translucent. Luster vitreous to greasy. Cleavage fair. Biaxial. Plane of the optic axes in the plane of symmetry. Birefringence strong.

Occurrence: As crystals on schist or as botryoidal stalactites at the pyrite mines of Szomolnok, Hungary.

Discussion: Isomorphous with kieserite. (Identical with ferropallidite.)

W. F. F.

Usbekite

I. Kurbatov and V. Kargin: Sur la Composition chemique d'une variété d'Ousbékite. (On the chemical composition of a variety of usbekite). *C. R. Acad. Sci. l'URSS.*, No. 75–80, 1927. (In Russian).

α-Usbekite: Color dark green. $2RO \cdot V_2O_5 \cdot 3H_2O$. Analysis: H_2O- 0.53, H_2O+ 12.98, MgO tr. CaO tr. MnO 0.44, ZnO none, NiO 0.84, CoO 0.06, CuO 30.37, PbO 0.15, Fe_2O_3 4.81, Al_2O_3 4.45, SiO_2 19.21, V_2O_5 26.42. Total 100,26, Sample impure.

β-Usbekite: Color pale green. $3RO \cdot V_2O_5 \cdot 4H_2O$. Analysis: SiO_2 9.95, Al_2O_3 49.07, Fe_2O_3 0.12, MnO 0.13, CaO 4.54, MgO tr., CuO 1.27, V_2O_5 1.08, H_2O- 19.22, CO_2 3.56, H_2O+ 10.96. Total 99.90.

W. F. F.

Tanatarite

J. J. Tanatar: Zur Frage über monokline Diaspore. *Bull. d. Geol.-Mineral. Assoz. Berginstitute z. Dnepro. Petrowsk.*, 1927. Abstr. *N. J. Ref.*, I. 146, 1928.

Tanatarite is monoclinic but with 2V 83°–84° and not 51°–60°. Plane of the optic axes parallel to the perfect cleavage.

W. F. F.